



# Simple fabrication of solid phase microextraction fiber employing nitrogen-doped ordered mesoporous polymer by *in situ* polymerization<sup>☆</sup>



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## ABSTRACT

A combination of nitrogen-doped ordered mesoporous polymer (NOMP) and stainless steel wires led to highly sensitive, selective, and stable solid phase microextraction (SPME) fibers by *in situ* polymerization for the first time. The ordered structure of synthesized NOMP coating was illustrated by transmission electron microscopy (TEM) and X-ray diffraction (XRD), and microscopy analysis by scanning electron microscopy (SEM) confirmed a homogenous morphology of the NOMP-coated fiber. The NOMP-coated fiber was further applied for the extraction of organochlorine pesticides (OCPs) with direct-immersion solid-phase microextraction (DI-SPME) method followed by gas chromatography–mass spectrometry (GC–MS) quantification. Under the optimized conditions, low detection limits (0.023–0.77 ng L<sup>-1</sup>), a wide linear range (9–1500 ng L<sup>-1</sup>), good repeatability (3.5–8.1%, *n* = 6) and excellent reproducibility (1.5–8.3%, *n* = 3) were achieved. Moreover, the practical feasibility of the proposed method was evaluated by determining OCPs in environmental water samples with satisfactory recoveries.

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## 1. Introduction

The ordered mesoporous polymers (OMPs) with mesoporous pores (*i.e.* 2–50 nm) and high-ordered architectures have attracted ever-growing attention due to their outstanding properties, such as controllable morphology, high specific surface areas, regular mesoporous structure and tunable pore size [1–3]. In addition, the properties of low weight and high flexibility make the OMPs complement their inorganic counterparts, such as mesoporous silica [4]. These significant advantages make the OMPs to be promising candidates in catalysis, sensing, membrane, adsorption and separation [5–7]. For instance, OMPs have been reported as excellent adsorbents toward many organic and inorganic compounds. While the adsorption performance of OMP is highly dependent on their various material parameters including specific surface area, functional group, and element, it is recently revealed that high nitrogen-content can result in high uptake and selectivity

simultaneously [8–10]. Therefore, nitrogen-doping as a fascinating method to change the performance of adsorptive materials has attracted worldwide attention recently.

Apart from the same advantages of OMP, the nitrogen-doped ordered mesoporous polymers (NOMPs) possess the polar surface and basic sites [11,12]. To date, various NOMPs have been calcined to prepare nitrogen-doped ordered mesoporous carbons (NOMCs) and the NOMCs have been extensively studied for carbon dioxide (CO<sub>2</sub>) adsorption because of the increasing concentration of CO<sub>2</sub> in the atmosphere in recent decades, which is believed to be the main reason of global warming and climate change [13–15]. However, there exist few works that NOMPs are regarded as adsorbents, but not the precursors of the NOMCs. In fact, NOMPs are potential to be excellent adsorbents for polar compounds due to the long-pair electrons and active basic centers.

Solid phase microextraction (SPME) is a green analytical technique for sample pretreatment technology first introduced by Pawliszyn [16] and has important advantages over conventional extraction techniques due to its simplicity, rapidity, sensitivity and easy quantification [17–19]. The key part of SPME is the adsorptive materials since the extraction process mainly depends on the high affinities between the adsorbent and adsorbate [20–22]. It is an effective way to improve the sensitivity and selectivity and low the cost of the SPME method by selecting appropriate adsorbent.

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Meanwhile, SPME can make the best of small amount of adsorbents and highlight the adsorptive properties of the adsorbents at normal pressure.

Hence, we synthesized the NOMP *via* self-assembly process using F127 (EO<sub>106</sub>–PO<sub>70</sub>–EO<sub>106</sub> triblock copolymer) as a soft template, low-molecular-weight resol as a carbon source, and hexamethylenetetramine (HMT) as a nitrogen source. We have confirmed that the OMP can be doped with nitrogen atom successfully to prepare the NOMP by the simple method and the ordered mesoporous structure was still kept well. Herein, the NOMP was employed as SPME fiber coating by *in situ* polymerization for the first time. The extraction capacity of the NOMP-coated fiber was investigated by comparing with those of the OMP-coated fiber and commercial PDMS fiber coupled with gas chromatography–mass spectrometry (GC–MS). It demonstrated that the nitrogen atom effectively enhanced the polarity of NOMP coating and made the NOMP-coated fiber trend to extract polar compounds, such as organochlorine pesticides (OCPs).

## 2. Experiments

### 2.1. Chemical and reagents

In the process of synthesis NOMP, the commercial triblock copolymer F127 (EO<sub>106</sub>–PO<sub>70</sub>–EO<sub>106</sub>) and phenol (≥99.5) were purchased from Aladdin (Shanghai, China). The sodium hydroxide (NaOH, A.R.), hexamethylenetetramine (HMT, A.R.), formaldehyde (w/v, 37%), hydrochloric acid (HCl, A.R.) and ethanol (A.R.) were purchased from Guangzhou chemical reagent factory (Guangzhou, China). Hexachlorobenzene (HCB, 99.5%), *trans*-chlordan (99.5%), *cis*-chlordan (99.5%), *o,p*-DDT (99.5%), *p,p*-DDT (99.5%) and mirex (98%) were bought from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

The commercial polydimethylsiloxane (PDMS, 30 μm) fiber was purchased from Supelco (Bellefonte, PA, USA) and the stainless steel wires were bought from Small Parts (Miami, FL, USA).

### 2.2. Instruments

The GC–MS (6890N-5975) system equipped with a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm) (Agilent technologies) and multipurpose sampler (MPS, Gerstel, Germany) was employed for the analysis procedure. The morphology of the NOMP-coated fiber was characterized by the scanning electron microscopy (SEM, Quanta 400F, FEI/OXFORD/HKL, Dutch). The elemental analyzer (EA, Vario EL, Elementar, Germany), X-Ray Diffractometer (XRD, D-MAX 2200 VPC, Rigaku, Japan), X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo-VG Scientific, America) and thermogravimetry (TG, TG 209 F3 Tarsus, Netzsch, Germany) were applied to characterize the synthesized NOMP coating.

### 2.3. Preparation of the NOMP-coated and OMP-coated fibers

According to the molar ratio of phenol/formaldehyde/NaOH = 0.61/0.39/0.026, 1.3 mL of 5 M NaOH solution and 10.4 g of 37 wt.% formaldehyde were added into 6.1 g melted phenol. Then, 1.22 g of HMT was added into above mixed solution. The mixed solution was stirred for 0.5 h at 70 °C and adjusted with 5 M HCl solution until the neutral phenol-formaldehyde resol solution was obtained. The prepared solution was diluted by ethanol and the constant volume was 100 mL. Then, 1.0 g F127 dissolved in ethanol was added into 10 mL of the as-made phenol-formaldehyde resol solution and the obtained solution was stirred at room temperature to promote the volatilization of the ethanol.

Then, the stainless steel wires were pretreated according to our previous work [20] prior to the coating procedure. The prepared

solution became viscous after the ethanol evaporated for several hours. The pretreated stainless steel wires were inserted into the viscous solution and kept for 10 min. Subsequently, the stainless steel wires were pulled out and an even layer of phenolic resin was coated on the surface of the stainless steel wire. Next, the coated stainless steel wire was placed in oven for 24 h at 100 °C for thermopolymerization. After that, the as-made fiber was further treated under N<sub>2</sub> flow at 350 °C for 6 h to obtain the NOMP-coated fiber.

To elucidate the influence of nitrogen atom, the OMP-coated fiber without nitrogen atoms was also prepared according to the reported work [21].

### 2.4. The direct immersion solid phase (DI-SPME) procedure

In all experiments, 10 mL of working solution or sample solution was transferred into a 10 mL glass vial and the NOMP-coated fiber was immersed into the solution to extract OCPs for a period of time at the selected extraction temperature. The extraction temperature was controlled by the incubator of the MPS. After reaching extraction time, the NOMP-coated fiber containing analytes from the sample, was withdrawn from the vial and inserted into the GC injector for thermal desorption.

### 2.5. Real water samples

The water samples were freshly collected (on November 2014) from Pearl River and the pond of Sun Yat-Sen University in Guangzhou, then placed at room temperature before use.

## 3. Results and discussion

### 3.1. Characterizations

#### 3.1.1. Characterizations of the NOMP coating

The structure of the NOMP coating was studied by XRD. Two diffraction peaks with a *d* spacing ratio of 1/(1/√2) were shown in low-angle X-ray diffraction patterns (Fig. 1a). It demonstrated that the NOMP coating possessed a typical body-centered cubic mesoporous structure, since the diffractions could be indexed as 110 and 200. The well-distributed ordered mesopores were generated from the thermo-decomposition of the soft template F127 at 350 °C, revealing the excellent thermal stability of NOMP coating to meet the requirements of the GC injector. The thermal stability was also proved by the thermal gravity analysis (TGA), as shown in Fig. 1b. It illustrated that there was a small amount of mass loss due to the removing of the adsorbed substance before 400 °C and existed obvious mass losses until 400 °C.

The EA was applied to analyze the composition element of the NOMP coating by the burning method and the XPS was efficiently employed for the chemical composition analysis on the NOMP-coated fiber surface (Fig. 2). From Fig. 2b, four Gaussian peaks with binding energies of 398.7 (N-6), 400.3 (N-5), 401.4 (N-Q), and 402–405 eV (N-X) [23] were observed, and the ratio of nitrogen to carbon (N/C) was 0.032, indicating that the OMP was doped with nitrogen successfully. From the EA results (Table 1), the N/C ratio was 0.015 in the NOMP coating. The N/C ratio by the EA method was smaller than that analyzed by XPS, it demonstrated that the nitrogen atoms were more distributed on the surface of the NOMP coating, which was benefit to promote the interactions between the nitrogen atom and selected analytes.

#### 3.1.2. Morphology feature of the NOMP-coated fiber

The surface morphology of the NOMP-coated fiber was characterized by SEM, as shown in Fig. 3. In the low magnification SEM

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